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TRANSITION METAL CARBIDES
Dependence of some thermochemical quantities on the chemical nature of reactants and stoichiometry of the product

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Abstract

Linear relationship were found among the plots of $\Delta H_{T_{ad}}$ and $\Delta G^0_{T_{ad}}$ *vs*. the adiabatic reaction temperature (T_{ad}) for transition metals carbides and silicides characterised by the same stoichiometry. The slope of the straight line depends on the product stoichiometry.

Keywords: adiabatic temperature, carbides, combustion synthesis, silicides

Introduction

In the transition metal carbides (groups IV B, V B and VI B) the non-metal atoms are located into the interstitial sites of the metal sub-lattice. All the IV B and V B carbides form MC compounds with a face centred cubic structure, while in the VI B group only MoC has this type of structure, WC having a simple hexagonal structure and CrC not existing. The sub-carbides M_2C have a hexagonal closest packed structure. In particular transition metal carbides are characterised by similar and extremely interesting combination of properties, such as high melting points and good mechanical properties also at high temperature. Moreover, most of them are stable in a quite wide homogeneity range, especially at high temperature; their properties strongly depend on and homogeneously vary with carbon to metal ratio. Their great stability reflects on the heat released during reaction between the metal and carbon, that is the reaction that leads to the formation of the carbide starting form the elements is strongly exothermic in most cases; for this reason some of them can be prepared by means of a self-sustained reaction (combustion synthesis, SHS technique) [1–4].

By means of the thermodynamic data it is possible to calculate the temperature reached during exothermic reaction carried out in adiabatic conditions (T_{ad}), that is without heat losses. Disregarding the phase transitions (solid state transition and/or melting) that the products may experience, the adiabatic temperature of the reaction may be calculated applying the equation [1–3, 5]:

$$-\Delta H^0 = \int_{298}^{T_{ad}} C_{ps}\,dT$$

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where ΔH^0 and C_{ps} are the enthalpy of formation at 298 K and the heat capacity of the product respectively.

In literature $\Delta H^0/C_p^0$ *vs*. T_{ad} diagrams are often reported [1–3] (C_p^0 is the heat capacity of the product at 298 K) and they are used as a guide to predict if the reaction can self-sustain or not. If the product does not melt during combustion then in general a linear relationship holds between these two parameters (that is $\Delta H^0/C_p^0$ and T_{ad}) for borides, carbides, silicides.

The aim of this paper is to study the relationship between $\Delta H^0/C_p^0$ and T_{ad} for materials belonging to a particular class of compounds, such as carbides and silicides in the present case, or characterised by the same stoichiometry. Moreover new linear relationships involving T_{ad} and some thermochemical quantities are introduced.

Results and discussion

Generally speaking the straight lines obtained plotting some thermochemical quantities ($\Delta H^0/C_p^0, \Delta H_{T_{ad}}$ and $\Delta G^0_{T_{ad}}$; $\Delta H_{T_{ad}}$ and $\Delta G^0_{T_{ad}}$ are respectively the enthalpy and the free Gibbs energy of the reaction calculated at the adiabatic temperature) *vs*. T_{ad} are characterised by different angular coefficients when carbides characterised by different stoichiometry, such as the mono-carbides MC and the sub-carbides M_2C, are separately considered. The slope of the straight lines is also different if different kinds of compounds characterised by the same stoichiometry, such as mono-carbides, MC, and mono-silicides, MSi, are compared. The thermodynamic data of carbides were taken from [6], while that of silicides from [7].

Figure 1 shows the linear relationships between $\Delta H^0/C_p^0$ *vs*. T_{ad} for MC and M_2C, while Fig. 2 for MC and MSi. Figures 3 and 4 show the linear relationship between $\Delta H_{T_{ad}}$ and $\Delta G^0_{T_{ad}}$ *vs*. T_{ad} for MC and M_2C.

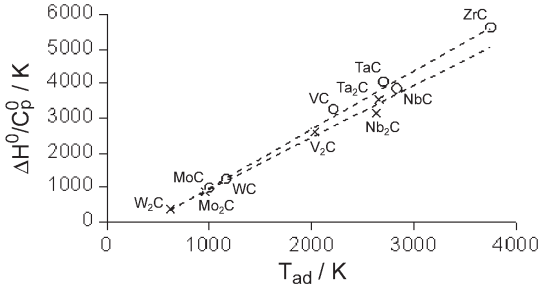

Fig. 1 Linear relationship between $\Delta H^0/C_p^0$ and T_{ad} for some transition metal carbides: MC mono-carbides (o); M_2C sub-carbides (×)

The angular coefficients of the obtained straight lines depend on the reaction stoichiometry and the type of the synthesised compound. Experimental observations led to the conclusion that the reaction can self-sustaining only when T_{ad}>1800 K [1–4]; from the graphics of Figs 3 and 4 it can be argued that the reaction leading to the formation of a

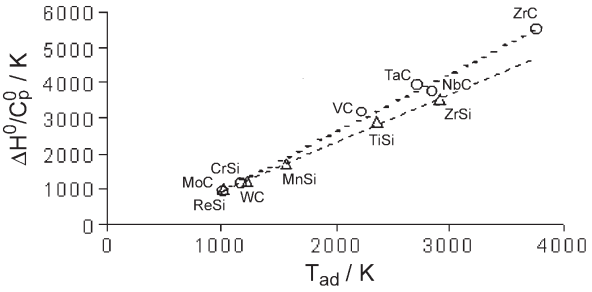

Fig. 2 Linear relationship between $\Delta H^0/C_p^0$ and T_{ad} for some transition metal mono-carbides (o) and mono-silicides (Δ)

mono-carbide MC will self-sustain when $\Delta H_{T_{ad}} < -83$ kJ mol^{-1} and $\Delta G^0_{T_{ad}} < -72$ kJ mol^{-1}; similarly the reaction that leads to the formation of a sub-carbide M_2C will self-sustain when $\Delta H_{T_{ad}} < -123$ kJ mol^{-1} and $\Delta G^0_{T_{ad}} < -119$ kJ mol^{-1}. If we consider MC and M_2C carbides of a particular transition metal, the difference between their adiabatic temperatures is little. It follows that the growth of the mono-carbide MC is favoured than that of the M_2C sub-carbides at adiabatic temperature.

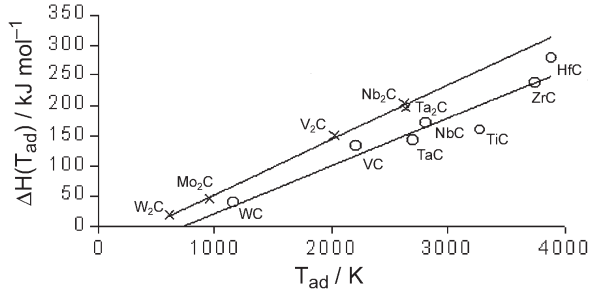

Fig. 3 Linear relationship between $-\Delta H_{T_{ad}}$ and T_{ad} for some transition metal carbides: MC mono-carbides (o); M_2C sub-carbides (×)

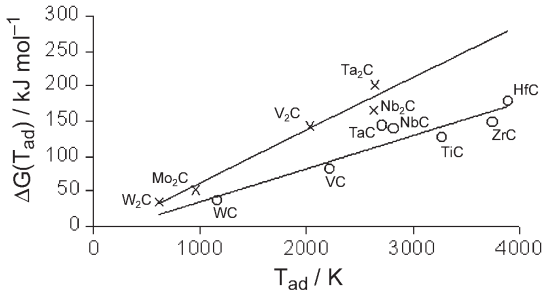

Fig. 4 Linear relationship between $-\Delta G^0_{T_{ad}}$ and T_{ad} for some transition metal carbides: MC mono-carbides (o); M_2C sub-carbides (×)

Conclusions

It has been found that linear relationships hold plotting the values of some thermochemical quantities ($\Delta H^0/C_p^0, \Delta H_{T_{ad}}, \Delta G_{T_{ad}}^0$) of transition metal carbides and silicides *vs*. T_{ad} In particular the slope of the straight lines calculated by means of the least square method depends on the nature of the reactants and the stoichiometry of the products.

From these graphics it can be argued that the reactions that lead to the formation of a mono-carbide MC staring from the elements can self-sustain only when $\Delta H_{T_{ad}} < -83$ kJ mol^{-1} and $\Delta G_{T_{ad}}^0 < -72$ kJ mol^{-1}; in the same way for M_2C sub-carbides must be $\Delta H_{T_{ad}} < -123$ kJ mol^{-1} and $\Delta G_{T_{ad}}^0 < -119$ kJ mol^{-1}.

References

1 Z. A. Munir, Cer. Bull., 67 (1988) 342.
2 H. C. Hy and J. J. Moore, J. Mat. Sci., 25 (1990) 1159.
3 J. J. Moore and H. J. Feng, Progr. Mat. Sci., 39 (1995) 243.
4 A. G. Merzhanov, Problems in Technological Combustion in Combustion Process in Chemical Technology and Metallurgy, Ed. by A.G.Merzhanov, Chernogolovka 1975.
5 J. B. Holt and Z. A. Munir, J. Mat. Sci., 21 (1986) 251.
6 O. Kubaschewski, C. B. Alcock and P. J. Spencer, Materials Thermochemistry, Pergamon Press, Oxford 1993.
7 S. B. Bhaduri, Z. B. Qian and R. Radhakrishnan, Scripta Met. Mater., 30 (1994) 179.